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(1) Patent Publication No. 96-310979

(19) Japan Patent Agency (12) Patent Publication Communique (11) Patent Pub.No.

Patent 96 - 310979

(43) Publication date: 26 November 1996

(51) Int.Cl.	Distinguishing Mark	Internal Reference	F1	Technology Disclosure Section
C07C	15/46	9546-4H	C07C 15/46	
	7/13		7/13	
	17/389		17/389	
	21/18		21/18	
	67/56		67/56	

Examination of Claims Pending Claims No. Claims: 5 FD (Total 14 Pages) Continued back page

(21) Application No. Patent Application 95-145368
(22) Application date: 19 May 1995

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(54) [Invention Title] Vinyl Monomer purification method.

(57) [Summary]
[Composition] A vinyl system monomer characterised by the elimination of adsorption of the polymerisation inhibiting agent in the above mentioned vinyl system monomer, when processing a vinyl system monomer which contains a polymerisation inhibiting agent.

[Result] If a vinyl system monomer purification method according to the present invention is adopted, the vinyl system monomer can be refined with the polymerisation inhibiting agent in the vinyl system monomer being eliminated very easily and reliably.

[Scope of Claims]
[Claim 1] A vinyl system monomer purification method characterised by eliminating the polymerisation inhibiting agent in the above mentioned vinyl system monomer by adsorption, when processing vinyl system monomer containing a polymerisation inhibiting agent.
[Claim 2] A purification method as mentioned in Claim 1 wherein the vinyl system monomer is an acrylic system, styrene system, vinyl acetate system, acrylo-nitride system or ethylene fluoride system monomer.
[Claim 3] A purification method as cited in claim 2 wherein the acrylic system monomer is an ester of (meta) acrylic acid with carbon 1~ 20 monovalent alcohol.
[Claim 4] A purification method as in claims 1, 2 & 3 above wherein the adsorbent is selected from alumina, silica gel, molecular sieve, activated carbon, ion-exchange resin, chelating resin, zeolite or acidic clay.
[Detailed Description of Invention]
[0001]
[Industrial Application Area]
The present invention is concerned with a process for refining vinyl system monomers to eliminate the polymerisation inhibiting agent which is contained in vinyl system monomers, particularly acrylic system monomers.
[0002]
[Prior art along with problems to be solved by the invention] In order to prevent polymerisation in vinyl system monomers during storage, particularly the acrylic system monomers available on the market, polymerisation inhibiting agents such as hydroquinone, acrylic substitute phenol are included in substantial amounts of 30 ~ 200 ppm. An acrylic system monomer containing a polymerisation inhibiting agent of this type, if trying to obtain a transparent polymer when polymerised, it is tinted by the polymerisation inhibiting agent, and because the visible light is absorbed the polymer light permeability is reduced. Due to this, it is desirable to remove the polymerisation inhibiting agent in the monomer and carry out polymerisation using a purified monomer.

[0003] With this type of monomer as a purification method, although there are distillation methods, and alkali extraction methods etc., the low boiling-point acrylic system monomer is nevertheless effective, but in the case of high boiling-point monomers the polymerisation inhibiting agent is extracted at the same time, the purity of the refined product being degraded, or the acrylic system monomer is not extracted, becoming impossible to distil. Additionally, if the distillation temperature is high, there is a danger that polymerisation will commence during distillation. On the other hand, with alkali extraction methods, the refinement effectiveness is inferior, and there is a problem in that it becomes difficult to obtain a high purity monomer.
[0004] The present invention takes the above mentioned circumstances into account, and therefore aims to offer a purification method for a vinyl system monomer which obtains a sure and simple elimination of the polymerisation inhibiting agent in vinyl system monomers.
[0005] [Steps and action in order to solve the problem] As a result of conducting diligent investigations in order to achieve the above mentioned objective, the inventor generated the present invention, from the knowledge based upon processing of vinyl system monomers, such as acrylic system monomers, with an adsorbent such as alumina, silica gel, molecular sieve, activated carbon, ion-exchange resin, chelating resin, zeolite and acidic clay, so that polymerisation inhibiting agents such as hydroquinone, alkali substitute phenol can be eliminated more effectively, particularly if alumina, silica gel etc, are used.
[0006] As a consequence, by processing the vinyl system monomer containing a polymerisation inhibiting agent with an adsorbent, the present invention offers a purification method for vinyl system monomers, characterised by the rapid elimination through adsorption of the above cited polymerisation inhibiting agent in vinyl system monomers.

[0007] Furthermore, with regard to the present invention, as illustrated in detail below, the purification method for the vinyl system monomer in the present invention is a method of eliminating the polymerisation inhibiting agent in the said monomer, when processing the said monomer with adsorbent.

[0008] Here the vinyl system monomer which forms the object of this process, usually contains > 1ppm polymerisation inhibiting agent such as hydroquinone type, alkyl substitute phenol, and in the present invention, a process for acrylic system monomer, or styrene system, vinyl acetate system, acrylo nitrile system, ethylene fluoride system monomers etc., which include an abundance of a particular polymerisation inhibiting agent is effectively employed, namely, >10ppm, especially > 50ppm, and above all > 100ppm. Furthermore, for the acrylic system monomer, acrylic acid, methacrylic acid, and esters of this acrylic acid, or methacrylic acid, with carbon 1 ~20 monovalent alcohol etc., are suitable for use, but above all, an ester of acrylic acid or methacrylic acid with carbon 8 ~ 20 monovalent alcohol high boiling-point is an ideal process.

[0009] Alumina, silica gel, molecular sieve, activated carbon, ion exchange resin, chelating resin, zeolite or acidic clay are suitable for the adsorbent which processes the above mentioned vinyl system monomer, among all these alumina, silica gel, activated carbon, molecular sieve are used ideally to maximum effectiveness in eliminating the polymerisation inhibiting agent.

[0010] An appropriate average particle size is selected for the above mentioned adsorbent, however 50 ~ 500 mesh, especially 100 ~ 300 mesh is desirable. These fine particles, processed into particular shape, can also be employed.

[0011] Methods such as the immersion method of impregnating vinyl system monomer with an adsorbent, or the column absorption method of passing vinyl system monomer through a column filled with adsorbent, can be used. In this case, the process can be kept the same for the vinyl system monomer, and if necessary, can also be diluted with hexane organic solvent, using the organic solvent as a carrier solution. However, the process temperature is assumed to be 0 – 150°C, and although the appropriate choice should depend upon the monomer viscosity, room temperature is usually adequate.

[0012] Using this kind of process, reducing the amount of polymerisation inhibiting agent in the vinyl system monomer to less than the original 50%, if this refined monomer, having a reduced amount of polymerisation inhibiting agent in this way, is used to polymerise the transparent polymer, and the polymer coloration is reduced as far as possible, the light permeability is high, and consequently this polymer is effective as the core material of a light transmission tube. Furthermore, the polymerisation method using this refined monomer is a well-known technique.

[0013] [Implementation example] An implementation example is shown below with a comparative example, and although it illustrates the present invention in essence, the present invention is not limited to this implementation example.

[0014] The adsorbent is used by packing absorbant cotton into a glass tube having a necked lower part of 3cm internal diameter, 10g of the adsorbent shown in table 1 is poured over this, with more absorbant cotton being packed above this. 100g of an acrylic system monomer SLMA (an ester of methacrylic acid with carbon 12 ~ 13 fat group monovalent alcohol) which includes 100ppm of metoxyhydroquinone as the polymerisation inhibiting agent (MEHQ), is processed by being poured through this (*translator's note: presumably 'the glass tube containing adsorbent'*), and the quantity of MEHQ in the outgoing liquid is measured as shown below. The results are shown in table 1.

MEHQ Measurement Method

2g of SLMA is dissolved into 3g of glacial acetic acid, 0.5ml of saturated sodium nitrous solution is added to colour it, and the adsorption strength is measured at 420nm. This value is compared with the data from the MEHQ value already known (calibration curve), and the MEHQ value (ppm) is obtained.

[0015] Next, the above mentioned outgoing liquid (refined monomer) is put into a 6mm diameter, 50cm long tube of FEP (Ethylene fluoride 4 propylene fluoride 6 copolymer) and 0.5 parts of benzoyl oxide to 100 parts acrylic monomer is used as the polymerisation initiator, and then after polymerising for 3 hours at 70°C, the polymer obtained is measured for transmissivity at 420 nm. The results are given side-by-side in table 1.

[0016]

[Table 1]

Adsorbent	MEHQ Amount In Outgoing Liquid (ppm)	Polymer Transmissivity (%)
Un-refined	100	0
Molecular Sieve 5A [Granule Type 1/16]	20	35
Silica Gel [100~200mesh]	15	40
Alumina [100~200mesh]	10	50
Activated Carbon [100~200mesh]	12	45

[0017]

[Result of Invention]

If the refinement method for vinyl system monomers according to the present invention is used, vinyl system monomers can be refined to eliminate the polymerisation inhibiting agent in the vinyl system monomer, both easily and surely.

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(51) Int.Cl.	Distinguishing Mark	Internal Reference	F1	Technology Disclosure Section
C07C 69/15			C07C 69/15	
69/54		9546-4H	69/54	Z
253/34			253/34	
255/08			255/08	
C08F 2/00	MAD		C08F 2/00	MAD
// B01J 20/08			// B01J 20/08	A
20/10			20/10	D
20/18			20/18	B
20/20			20/20	B

Patent Abstracts of Japan

PUBLICATION NUMBER : 08310979
PUBLICATION DATE : 26-11-96

APPLICATION DATE : 19-05-95
APPLICATION NUMBER : 07145363

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INT.CL. : C07C 15/46 C07C 7/13 C07C 17/389 C07C 21/18 C07C 67/56 C07C 69/15 C07C 69/54 C07C253/34 C07C255/08 C08F 2/00

TITLE : PURIFICATION OF VINYL MONOMER

ABSTRACT : PURPOSE: To purify a vinyl monomer by easily and surely removing polymerization inhibitors in a vinyl monomer.

CONSTITUTION: A vinyl monomer such as acrylic, styrene, vinyl acetate, acrylonitrile or fluorinated ethylene monomer is treated with an adsorbent such as alumina, silica gel, molecular sieve, activated carbon, ion-exchange resin, chelate resin, zeolite and acid clay. The adsorption treatment is carried out e.g. by the immersion process comprising the impregnation of the adsorbent into the vinyl monomer or the column adsorption method comprising the packing of a column with the adsorbent and the passing of the vinyl monomer through the column. The vinyl monomer may be treated with the adsorbent as it is, diluted with a solvent such as hexane or used as a carrier liquid. The treating temperature is 0-150°C, usually room temperature. The amount of the polymerization inhibitor is decreased to ≤50% of the original content by this adsorption treatment. The transparent polymer produced by polymerizing the refined monomer has minimized color and high light transmittance and is usable as a core material of a light-transmission tube.